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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "What effect does VOC sampling time have on derived OH reactivity?" *by* H. Sonderfeld et al.

Anonymous Referee #2

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The manuscript "What effect does VOC sampling time have on derived OH reactivity?" presented by Sonderfeld et al. is an extended analysis of two different field campaign's high resolution data-sets with regard to the question if and how strong different sampling times and intervals impact the calculation of missing OH reactivity. This question is of relevance for understanding atmospheric photooxidation processes especially when the directly measured total OH reactivity and the budget of individually detected OH sinks such as volatile organic compounds (VOC) are compared. For example, gas chromatographic samples are often collected over a time spanning several minutes whereas the actual analysis of the sample can be as long as one hour. Sonderfeld et al. explore methodically whether a comparison between such low and high resolution data-sets might miss-represent the true variability and average value of the atmospheric observations with respect of the overall OH reactivity.

Overall, the data-sets discussed in this manuscript are taken from recent field measurements campaigns, the analysis has been explained carefully, the results are well presented, and the overall conclusions aim to answer the question which was raised within the title. I recommend this paper for publication in ACP and have the following minor specific, general and technical comments.

Specific comments:

SC 1) p.3, l.10- p.4, l.6: The authors present a very good compilation of studies about missing OH reactivity based on the comparison of individually measured OH sinks and the directly detected total OH reactivity. As stated later in the introduction (paragraph p.4, l.14-22) the different time resolutions of OH reactivity and individual compound measurements might bias the comparison hence the resulting missing OH reactivity. With this in mind and following the scope of the entire manuscript, it would be interesting for the reader to get some information about typical instrumentation (e.g. GC) and sampling times (e.g. first 10 min of a 40 min cycle) that have been used for VOC measurements and compared to the directly detected total OH reactivity. Is it possible to include this additional information, either for all or some of the examples that are provided in the text already?

SC 2) p.3, l.28-29: Indeed both of the studies presented here concluded that the missing OH reactivity is possibly due to unmeasured oxidation products. However, they did not exclude the contribution of undetected forest emissions that may add to the missing reactivity, as well.

SC 3) p.5, l.14-15 and p.7, l. 9: For both measurement campaigns that are chosen for presenting data in this manuscript a calibration was performed before (and for PARADE also after) the campaign. Was the calibration done at the measurement site or in the laboratory?

SC 4) Table 2: How did you calculate the accuracy as error for the measurements? Why did you chose 1sigma for the ClearfLo campaign and 2.6sigma for the PARADE campaign as LOD?

SC 5) p.11, l.2-3: Since the different monoterpenes have very different reactivities towards OH, it is critical to know their atmospheric composition for calculating the OH reactivity due to monoterpenes. Especially the two contrasting sites presented here might have very different typical ambient monoterpene distributions resulting in different characteristic OH reactivities. Unfortunately, the PTR-MS cannot separate the different monoterpenes and detects all of them as one single signal. Therefore, the authors decided to use the reaction rate of a-pinene only. In case that during the campaigns the monoterpene composition was characterized by accompanying instrumentation (e.g. GC-MS) could you use that data to estimate a typical monoterpene OH reaction rate coefficient? Or in case that you did not have such observations during the campaign, are there any studies in the literature that could give you hints about the typical monoterpene distribution at the campaign sites? A typical monoterpene composition will help you to estimate a typical monoterpene reaction rate with OH that is representative for location and timing of the two campaigns.

SC 6) p.12, l.19: Why do you need to generate a randomized data set? What do we learn from comparing this fictive distribution of OH reactivities to the field data?

SC 7) p.14, l.20-28 and p.16 Table 5: Could you please explain why you chose to not include ΔR in Table 5? The standard deviation of ΔR is used as a measure of variance and presented in Table 5. However, I wonder if it would be more accurate to look at the standard deviation relative to the hourly average ΔR? Also, could you please clarify the physical meaning of the values presented by the Gaussian Fit Centre and the FWHM (full width at half maximum)? You say that the Gaussian function was fitted on the frequency distribution of the ratio of shorter interval averages (R(t<60)) to the hourly average (R(t=60min)). In this case a value of 1 would be calculated for perfect overlap of those two averages and the FWHM would convert to zero, right?

SC 8) p. 16, l. 7-8: These two sentences seem to have contradicting statements: The

small standard deviation of ΔR highlights the narrow range of calculated OH reactivity. And the high variability of the data is reflected by the relatively high FWHM. Could you please explain? Would you get a different result if looking at the relative standard deviation?

SC 9) p.18, l.12-15: A more general remark in this context: It could be interesting, regarding the discussion about the difference of variabilities at the two different sites, to have a look at the variability-lifetime relationship as for example presented in Williams et al. 2000 (http://dx.doi.org/10.1029/2000JD900203). Similarly for section 3.4 in which the effect of different VOC classes on OH reactivity is discussed.

SC 10) p. 26, Figure 13: The effect of VOC variability on the calculated OH reactivity is presented in this figure for the ClearfLo campaign. How does it look like for the PARADE campaign data? Are there significant differences?

SC 11) p. 28, l. 4-5: The missing variability in VOC data, that you mention here, is only due to the short interval sampling time. Is this correct?

SC 12) p. 28, l.5-6: The divergence between 5 min and 60 min averaged calculated OH reactivity is given here to be between 1-28% (PARADE) and 0-44% (ClearfLo). These numbers appear in the text for the first time at this point within the conclusions. Could you please include some reference in the text beforehand? And also it would be good to stronger point out the conditions and the statistical test (e.g. first 5 min of hour, consecutive 5 min intervals, regression methods, number of data points, effect of different VOC classes, . . .) that lead to the greatest divergence.

General comments:

GC 1) Within the presented study you solely compare VOC data with the OH reactivity calculation based on the measurement of individual OH sink compounds. Do you have any directly measured total OH reactivity data available to compare to?

GC 2) For the statistical analysis of the two field campaigns (ClearfLo and PARADE) the entire data-set was used. How does your overall conclusion depend on the time of the day? Did you test the small sampling interval averages against the hourly averaging for example for day and nighttime data only? Is it possible that some VOC show decreased variability within the nocturnal boundary layer whereas during daytime the close distance to emission sources and turbulent mixing increase their overall variability?

Technical comments:

TC 1) p.2, l.10: “Its actual concentration being determined by the balance between its sources and sinks.” It seems to me that the verb in this sentence needs to be “is” rather than “being”.

TC 2) p.2, l.17: Here, a list of references about in-situ measurements of OH reactivity is provided. However, it should be indicated (e.g. with “e.g.”) that this list only presents a fraction of the actual literature.

TC 3) p.3, l. 10: “. . . good agreement between measured and calculated OH reactivity have been found.” It should be “has” instead of “have”.

TC 4) Table 1: Are here averages or median values presented for the mixing ratios and concentrations? What is the given uncertainty? Standard deviation?

TC 5) p.7, l.25: I think you do not need the “whether” in this sentence.

TC 6) p.8, l.8: Here you repeat yourself by having “values” twice in one sentence.

TC 7) p.10 Figure 2: It would be great, if you could add a legend to the two graphs explaining the different markers used.

TC 8) p.10 Table 3: Table 3 basically repeats what is shown in Figure 2. I wonder if it is really necessary to include the same information twice. You might want to decide whether to present the figure or the table. Also, what units did you use to present the range of VOC mixing rations in Table 3?

TC 9) p.11 Table 4: Please correct the format of the VOC reactivity unit. Also, to be precise it is the OH reactivity due to the selected VOC.

TC 10) p.12, section heading and terminology: The term “VOC reactivity” can be misleading because atmospheric VOC typically react with various oxidants such as O3, NO3, Cl or OH. Hence, it is more precise to use the terminology OH reactivity. This applies already for most of the presented manuscript (e.g. Title, Figure 3 ect.) but should be checked for consistency, especially in this section 2.2.

TC 11) p.12, l.13: In the previous section you define the notation for different OH reactivity calculations which depends on the instrumentation, campaign and compounds taken into account. The example shows that OVOC during the ClearfLo campaign only includes acetone. Probably during the Parade campaign it would also include methanol. Then in section 2.2 the OH reactivity was calculated for VOC detected by GC during the ClearfLo campaign. However, what do you mean with TVOC as referred to in line 13?

TC 12) p.18, l. 20-21: Here, it is referred to Figure 4, which shows the randomly generated data set. In the context of presenting residual slopes as in Figure 9, I found this confusing and it might be a mistake. Also, from this point on you look at the residual slopes (as plotted in Figure 9). In the figures and sections before (e.g. Fig. 6, 7, 8) the slope was shown. Is there a reason for not being consistent about that?

TC 13) p. 24, Table 9: With “Random numbers” do you mean the “Randomly generated data set”?

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